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(54) Title: <b>PROCESS FOR RECOVERING MINERALS AND COMPOSITIONS FOR USE IN THIS</b>		
(57) Abstract <p>The invention provides a process of separating minerals from a mineral-containing material by froth flotation comprising forming an aqueous pulp of particles of the mineral-containing material, subjecting the pulp to flotation in the presence of one or more dialkyl thionocarbamate collectors, allowing preferential separation of the particles in the pulp to occur to form Reject and Accept fractions and separating the Reject and Accept fractions. In this process dialkyl thionocarbamate collector is added to the mineral-containing material or pulp in the form of an oil-in-water emulsion comprising dialkyl thionocarbamate collector in an amount of 5 to 95 wt.%, emulsifier in an amount of 1 to 30 wt.% and water in an amount of 5 to 95 wt.%. The dialkyl thionocarbamate emulsion is also a novel product.</p>		

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**PROCESS FOR RECOVERING MINERALS AND COMPOSITIONS**  
**FOR USE IN THIS**

The invention relates to an improved composition of dialkyl thionocarbamate collectors and use of this composition in a process of beneficiation of mineral-containing materials.

It is well-known to beneficiate crude mineral ores and other mineral-containing materials by froth flotation processes. These processes are used to separate a desired mineral from unwanted minerals which are unavoidably extracted in the mining operation with the desired mineral. It is also possible to use froth flotation systems to separate two or more desired minerals from a single crude ore or other mineral-containing material.

In a froth flotation process the mineral-containing material in particulate form is formed into an aqueous pulp. If the mineral-containing material is a crude ore it is generally ground to a particle size small enough that discrete particles of the required minerals are present. Some mineral-containing materials, such as coal, are particulate when they reach the flotation stage of processing.

The pulp is subjected to flotation to induce preferential separation of the particles in the pulp to form Reject and Accept fractions. Usually the Accept fraction is the surface fraction formed during the flotation process.

Dialkyl thionocarbamate collectors are often included in the pulp, either by addition directly to the aqueous pulp or by addition to the mineral-containing material during grinding, if used, to enhance separation.

Other collector materials are known. Water-soluble collectors are generally most conveniently added to the aqueous pulp of ground ore in the form of a solution, at around 5 to 10% concentration. Generally they are sold in the solid form or, less commonly, as a concentrated solution, and diluted on site. It is also known to use

some water-insoluble materials as collectors in the form of an oil-in-water emulsion.

Dialkyl thionocarbamate collectors are normally water-insoluble and are usually added neat, either singly or as a blend with other collectors. This is accepted as generally convenient. In particular neat dialkyl thionocarbamate collector can be added at the grinding stage, although it is also known to add it to the aqueous pulp. It is generally accepted within the industry that this form of application gives adequate results, in particular where neat collector is added at the grinding stage.

Aqueous compositions containing certain types of thionocarbamate collector have been described in the literature. For instance in US 3,925,218 and US 4,040,950 it is stated that N-alkyl O-alkyl thionocarbamate can be caused to dissolve in an aqueous solution of a dialkylthiophosphate salt. CA 1,105,156 describes dissolution of N-alkyl O-alkyl thionocarbamate in an aqueous solution of dialkyldithiophosphate. Such systems provide an alternative method of dosing the water-insoluble dialkylthionocarbamates. However the water-insoluble dialkylthionocarbamate must be added in combination with the water-soluble collector which allows it to be solubilised in the aqueous solution.

In AU 8543817 a composition is described which comprises a phosphorodithioic compound, a dialkylthionocarbamate and optionally an alkyl xanthogen alkyl formate. This mixture is described as being "water-emulsifiable". However, the patent suggests that only dispersion directly into water is used, and continuous agitation of the storage facility is required to maintain the water-insoluble mixture in dispersion. It is also indicated that the presence of a phosphorodithioic compound is essential to render the dialkylthionocarbamate dispersible. Such a system requires rather long periods to achieve efficient mixing, necessitates a make-up tank and

agitation facilities and places restrictions on the point of addition of the collector.

It is also known, for certain other water-insoluble collectors, particularly those used in the coal industry, to blend these with emulsifiers before adding this blend to the flotation stage. This is believed to assist in distributing collector onto the surface of coarse particles, rather than fine particles only.

A specific system of this general type for use in processing of metallic mineral ores is demonstrated in U.S. 4,211,644, in which mercaptan collector is mixed with an emulsifying agent before addition to the pulp, in order to improve dispersion of the mercaptan into the pulp. The mercaptan may be used together with other collectors which include thionocarbamates, but these other collectors are not included in the mixture of mercaptan and emulsifier.

A similar system is described in U.S. 4,526,696, in which certain collectors are provided as a mixture with surfactant and cosurfactant. This mixture is said to render the collector "microemulsifiable", that is it forms a microemulsion on addition to the mineral pulp. The collectors for which this system is said to be suitable are mercaptans, thioethers and polysulphides. It is suggested that handling can be facilitated by including water in the composition, although it is not indicated whether or not the resulting aqueous composition is an emulsion of any type.

The present invention is concerned with improvement of the performance of thionocarbamate collectors specifically. For instance it would be desirable to improve the recovery and selectivity performance of these collectors.

According to the invention we provide a process of separating minerals from a mineral-containing material by froth flotation comprising

forming an aqueous pulp of particles of the mineral-containing material,

subjecting the pulp to flotation in the presence of one or more dialkyl thionocarbamate collectors,

allowing preferential separation of the particles in the pulp to occur to form Reject and Accept fractions

5 and separating the Reject and Accept fractions, characterised in that dialkyl thionocarbamate

collector is added to the mineral-containing material or pulp in the form of an oil-in-water emulsion comprising dialkyl thionocarbamate collector in an amount of 5 to 10 95wt%, emulsifier in an amount of 1 to 30wt% and water in an amount of 5 to 95wt%, based on total emulsion.

The collector emulsion is also a novel product in itself. Thus the invention also provides a collector composition which is an emulsion of dialkyl thionocarbamate 15 collector in water and which comprises 5 to 95wt% dialkyl thionocarbamate collector, 1 to 30wt% emulsifier and 5 to 95wt% water, based on total emulsion.

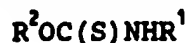
We find that the application of dialkyl thionocarbamate collector in the emulsion form produces 20 surprising improvements in performance of these collectors. Recovery of desired minerals can be improved, as can selectivity for the desired mineral over undesired minerals. We also believe that the efficiency of these collectors can be improved. That is, lower doses of the 25 collector in emulsion form would produce equivalent or better results than higher doses of the collector in neat form.

In particular we find that the dialkyl thionocarbamate emulsions of the invention give improved results in 30 comparison with mixtures of thionocarbamate and emulsifier, and in comparison with neat dialkyl thionocarbamate added simultaneously with a mixture of emulsifier and water.

We find additionally that the use of dialkyl thionocarbamate collector in the emulsion form provides a 35 convenient method of diluting the collector and thus provides for greater accuracy of dosage. Dosage can be at any convenient point in the flotation process, including

the flotation chamber. Emulsions of collector can be stored and used without the need for specialised storage facilities, which are required according to AU 8543817.

The process and product of the invention require a dialkyl thionocarbamate collector. Any water-insoluble dialkyl thionocarbamate collector may be used which is appropriate for the beneficiation of the crude ore being processed. Dialkylthionocarbamates have the formula



10  $R^1$  and  $R^2$  are alkyl groups of any suitable chain length but are preferably C1 to C6 alkyl groups, more preferably C1 to C4 alkyl groups. Ethyl and propyl, especially isopropyl, groups are preferred. Particularly preferred dialkylthionocarbamates have the above formula in  
15 which one of  $R^1$  and  $R^2$  is isopropyl and the other is ethyl. Especially preferred is isopropyl ethylthionocarbamate ( $R^1$  is ethyl and  $R^2$  is isopropyl). Mixtures of dialkyl thionocarbamates may be used.

A dialkyl thionocarbamate collector is normally water-  
20 insoluble, that is it will generally have solubility in water of 4g collector per 100g deionised water or below, often 1g collector per 100g deionised water or below.

The collector emulsion contains one or more dialkyl thionocarbamates in a total amount in the range around 5 to  
25 around 95%, preferably around 20 to around 80%, more preferably around 35 to around 70, more preferably up to 55%, often around 45%, by weight of emulsion.

The emulsion contains emulsifier in amounts in the range from around 1 to around 30%, preferably around 1 or  
30 2 to around 20%, often around 10%, by weight of emulsion.

Standard surfactant emulsifiers may be used, for instance alkoxylated alcohols and fatty acids, ethoxylated fatty amines and fatty diamines, quaternary fatty ammonium compounds, alkyl benzenesulphonates and alkyl sulphates and  
35 mixtures thereof. Preferred emulsifiers are ethoxy (20) sorbitan monolaurate and ethoxy (100) stearic acid, in particular a 50:50 (weight) blend of these.

The remainder of the emulsion is usually water. This is generally present in an amount of from around 5 to 95%, often around 20 to around 80%, preferably around 35 to around 55%, often 45% or less by weight of the emulsion.

5       The ratio of dialkyl thionocarbamate to water in the emulsion is preferably from 9:1 to 1:9, more preferably from 3:1 to 1:3, most preferably from 2:1 to 1:2, often around 1:1.

10       The ratio of dialkyl thionocarbamate to emulsifier in the emulsion is preferably below 9:1, and can be below 8:1 or below 5:1.

In this specification we include within the term "emulsion" systems in which the oily (collector) domains are of any size, and in particular we include systems of  
15       the type which are often referred to as microemulsions.

20       The dialkyl thionocarbamate emulsion of the invention is preferably formulated so as to be stable, and in particular it preferably remains stable (that is, the emulsion does not break and separate), without the need for continuous agitation, for at least half an hour, preferably at least 24 hours, more preferably at least one month and even as long as 3 months or more, for instance at least 12 months.

25       Some instability can be tolerated however provided the emulsion does not freeze on storage and provided it can be agitated to form a new emulsion easily before addition to the process.

30       The emulsion may contain components in addition to the water, emulsifier and dialkyl thionocarbamate collector. For instance it may contain water-soluble collector materials in the aqueous phase. Preferably any such materials are not such that they are cosolvents for the water-insoluble collector or collectors. That is, they do not induce solubility of the water-insoluble collector in  
35       the aqueous phase. It may, alternatively or additionally, contain other water-insoluble collector in minor amounts.



Preferably however the emulsion consists essentially only of water, emulsifier and dialkylthionocarbamate collector.

The dialkyl thionocarbamate emulsion can be prepared using standard emulsion preparation techniques.

5        The dialkyl thionocarbamate emulsion, which can comprise one or more additional types of collector, can be used as the sole source of collector in the process. Alternatively it may be used in combination with collector provided in different forms. For instance it may be used  
10       together with water-soluble collector in aqueous solution or water-insoluble collector added in the neat form. Collector added in forms other than as an emulsion can be added at any convenient stage of the separation process.

      Amounts of dialkyl thionocarbamate emulsion and  
15       collector in any other form if used are chosen to give a total level of added collector which is in the range 2 to 3000 g/t, based on dry weight of the aqueous pulp of ground ore, preferably 5 to 1500 g/t, often 10 to 200 g/t. Preferably amounts of dialkyl thionocarbamate in these  
20       ranges are used.

      The collector emulsion itself is usually included in a total amount of 2 to 4000 g/t, preferably 2 to 3000 g/t, more preferably 5 to 1500 g/t, based on dry weight of the pulp of ground ore.

25       The mineral-containing material to be treated by the froth flotation process is provided in particulate form. Some materials, such as crude mineral ores, are ground, usually to a particle size small enough that discrete particles of the individual minerals are produced. These  
30       particles are usually of a size 80% below 150 $\mu$ m, often 80% below 75 $\mu$ m. Grinding can be carried out by for instance rod or ball milling.

      If desired, a portion of the collector emulsion can be added to the ore at the grinding stage. Preferably however  
35       substantially all of the collector emulsion is added to the aqueous pulp. Crude ores are usually ground in the form of a slurry of solids content around 40 to 70%.

Materials such as coal are already in particulate form when passing to flotation and do not require grinding. Such materials passing to flotation usually have a particle size of around 80% below about 750 $\mu$ m.

5       The particulate mineral material is formed into an aqueous pulp. This requires adding water to materials such as coal which do not require grinding. For ground ores, which are in the form of a slurry after grinding, further water may be added if required. Solids content of the  
10       aqueous pulp is usually from around 8 to 40%, often around 10 to 35%. Coal is usually subjected to flotation in the form of an aqueous pulp of solids content around 10% and ground mineral ores are often subjected to flotation in the form of an aqueous pulp of solids content around 20 to  
15       around 35%.

Collector emulsion can be added to the aqueous pulp. It is also possible to include other collectors in other forms, for instance in aqueous form, if these are required. Other components which may be added to the pulp include  
20       frothers, sulphidising agents, gangue depressants and pH modifiers.

The aqueous pulp is then subjected to flotation, usually by aeration and optionally agitation, in a flotation chamber. As air bubbles travel through the  
25       aqueous pulp to the surface the collector enhances the natural tendency of selected minerals to adhere to the air bubbles, usually by modifying the surface properties of the particles of these selected minerals. The chosen minerals then preferentially adhere to the air bubbles and are  
30       carried to the surface of the pulp. If the selected minerals are those which are required to be recovered, this surface fraction is the Accept fraction, which can be separated for further treatment if necessary. Alternatively the selected minerals in the surface fraction may be those  
35       which are not required (the Reject fraction) and are separated and dumped. Generally however it is the valuable minerals which are floated and collected as the Accept

fraction as a concentrate. Occasionally selectivity is adequate after a single flotation. More commonly however two or more sequential flotations are required before the desired degree of ore refinement is obtained.

5 Two or more different collectors may be used in a single process, either to improve selection of a single mineral, or to allow separation from a single ore of two or more different minerals.

10 The process of the invention may be used in the beneficiation of any crude mineral ore, for instance those of zinc, copper, lead and nickel (in the form of sulphides or oxides), gold and silver and industrial minerals such as apatite and fluorspar. It may be used for the extraction of coal and graphite.

15 The invention will now be illustrated with reference to the following example.

Example

20 A crude zinc-containing ore was air dried for two days. It was then crushed and sieved at 500  $\mu\text{m}$  with the oversize being returned to the jaw crusher. The below 500 $\mu\text{m}$  fraction was coned, quartered and riffled to produce 1 kg lots.

25 1 kg of ore, together with 540  $\text{cm}^3$  of tap water, 250 g/tonne  $\text{ZnSO}_4$  (10% w/v) and 7.5 g/tonne sodium isopropyl xanthate (SIPX) (0.1% w/v), were added to a laboratory rod mill and milled for 5.75 minutes to produce a particle size of 63% below 75 $\mu\text{m}$ . The milled sample was then transferred to a 2.5 litre Denver flotation cell to await testing.

Initially a lead flotation procedure was carried out.  
30 3.0 g/tonne SIPX (0.1% w/v) and 17.5 g/tonne (1 drop) methyl isobutyl carbinol (MIBC) were added and conditioned for 1 minute at 1,200 rpm. The air was turned on and the froth produced was removed every alternate 10 second interval over a 3 minute period to produce the first  
35 concentrate. The air was turned off. 1.5 g/tonne SIPX (0.1% w/v) and 17.5 g/tonne (1 drop) MIBC were added and conditioned for 1 minute. Air was turned on and the froth

produced was removed as before over a 3 minute period to produce the second concentrate. Air was turned off. 1.5 g/tonne SIPX (0.1% w/v) and 8.8 g/tonne (half a drop) MIBC were added and conditioned for 1 minute. Air was turned on and the froth produced was removed as above over a 4 minute period to produce the third concentrate. Air was turned off. Amounts of SIPX and MIBC the same as the last addition were added and conditioned for 1 minute. Air was turned on and the froth produced was removed as above over a two minute period to produce a fourth concentrate. Air was turned off. The same amounts of SIPX and MIBC as in the last addition were added and conditioned for 1 minute. Air was turned on and the froth produced was removed as above over a two minute period to produce a fifth concentrate. Air was turned off. The five concentrates were individually filtered, dried and weighed for analysis.

The zinc flotation procedure was then carried out. Pulp pH was adjusted to 10.5 with lime,  $\text{Ca(OH)}_2$ . 375 g/tonne  $\text{CuSO}_4$  (10% w/v) was added and conditioned for 3 minutes. Air was turned on and the froth produced was removed every alternate 10 second interval over a 2 minute period to produce the first concentrate, Zn 1. Air was turned off. Pulp pH was readjusted to 10.5 with lime. 20.1 to 20.2 g/tonne active potassium amyl xanthate (PAX) in the form of a 1.0% w/v aqueous solution and 10.0 to 10.1 g/tonne collector emulsion (product A, see below) and 17.5 g/t (1 drop) MIBC were added and conditioned for 1 minute. Air was turned on and the froth produced was removed as above over a 3 minute period to produce the second concentrate, Zn 2. Air was turned off. Pulp pH was readjusted to 10.5 with lime. Half the original addition of product A (collector emulsion and PAX) was added followed by 8.8g (half a drop) MIBC and then conditioned for 1 minute. Air was turned on and the froth produced was removed as above over a 3 minute period to produce the third concentrate, Zn3. Air was turned off. Pulp pH was readjusted to 10.5 with lime. Half the original addition

of product A (collector emulsion and PAX) was added followed by 8.8 g (half a drop) MIBC and then conditioned for 1 minute. Air was turned on and the froth removed as above over a 3 minute period to produce the fourth concentrate, Zn4. The four concentrates were individually  
5 filtered, dried and weighed prior to analysis.

Concentrates Zn 1 and Zn 2 were analysed together.

The process was repeated with products B, C, D, E and F, described below. The amounts specified refer to the  
10 original addition between concentrates Zn 1 and Zn 2.

Product A: 20.1 to 20.2 g/tonne PAX + 10.0 to 10.1 g/tonne of an emulsion containing  
4 5 parts by weight isopropylethylthionocarbamate, 45  
15 parts by weight water and 10 parts by weight emulsifier

Product B: 20.3 g/tonne PAX + 5.6 g/tonne of a mixture of 45 parts by weight water and 10 parts by weight emulsifier

20 Product C: 20.4 g/tonne PAX + 4.6 g/tonne neat isopropylethylthionocarbamate

Product D: 20.1 to 20.2 g/tonne PAX + 4.5 to 4.6  
g / t o n n e n e a t  
25 isopropylethylthionocarbamate and, added separately, 5.5 to 5.6 g/tonne of a mixture of 45 parts by weight water and 10 parts by weight emulsifier.

Product E: 20.1 to 20.3 g/tonne PAX + 5.5 to 5.6  
30 g/tonne of a mixture of 45 parts by weight isopropylethylthionocarbamate and 10 parts by weight emulsifier.

Product F: 20.1 to 20.2 g/tonne PAX.

The emulsifier system used was a 50/50 (wt/wt) blend  
35 of ethoxy (20) sorbitan monolaurate and ethoxy (100) stearic acid.

Results are shown in Tables 1 and 2 below.

Table 1

Flotation time/mins	Cumulative Zinc Recovery, %					
	A	B	C	D	E	F
5 (Zn 1 + Zn 2)	86.7	22.2	32.8	36.6	42.0	33.4
8 (Zn 3)	97.3	52.7	61.5	64.8	69.5	62.1
11 (Zn 4)	98.6	78.9	89.2	92.9	86.7	82.9

5

Table 2

Flotation time/mins	Cumulative Zinc Grade, %					
	A	B	C	D	E	F
5 (Zn 1 + Zn 2)	57.0	53.7	56.1	53.3	37.3	39.0
8 (Zn 3)	47.5	63.4	54.2	49.6	36.6	41.3
11 (Zn 4)	42.8	53.6	48.7	44.3	33.4	39.2

10

The above results show the surprising benefits of using the invention (Product A). Product A shows excellent zinc recovery. In particular it shows excellent recovery in the early stages of the flotation. In a commercial flotation process the speed with which acceptable separation can be achieved is particularly important. The 5 minute values (Zn-1 + Zn-2) are particularly illustrative of this point. Product A shows excellent recovery and selectivity (cumulative zinc recovery and cumulative zinc grade, respectively) at this stage and is superior in both respects to all other products. In particular it is superior to a simple blend of collector and emulsifier.

At the later 8 minute and 11 minute stages the product of the invention shows recovery superior to all other products. In addition, it does not undergo significant reduction in the selectivity achievable. Thus it can be seen that the use of the invention allows achievement of rapid recovery with high selectivity and, in the long term, higher recovery combined with adequate selectivity. This combination of features is not achieved with any of the Products B to F.

It is particularly noticeable that the thionocarbamate emulsion (in Product A) gives improved results in comparison with Product E, which is a mixture of the collector and emulsifier. This is particularly unexpected in view of prior art suggestions to improve performance of other types of collector by mixing them with emulsifier alone. Addition of extra water together with the thionocarbamate is again not as effective as the thionocarbamate emulsion used in Product A. In particular, Product D includes, simultaneously with but separately from the thionocarbamate, amounts of water and emulsifier equivalent to those included in Product A but gives inferior results to those shown by Product A, in particular in recovery values.

CLAIMS

1. A process of separating minerals from a mineral-containing material by froth flotation comprising forming an aqueous pulp of particles of the mineral-containing material,  
5       subjecting the pulp to flotation in the presence of one or more dialkyl thionocarbamate collectors, allowing preferential separation of the particles in the pulp to occur to form Reject and Accept fractions,  
10       and separating the Reject and Accept fractions, characterised in that dialkyl thionocarbamate collector is added to the mineral-containing material or pulp in the form of an oil-in-water emulsion comprising dialkyl thionocarbamate collector in an amount of 5 to  
15       95wt%, emulsifier in an amount of 1 to 30wt% and water in an amount of 5 to 95wt%.  
2. A process according to claim 1 in which the oil-in-water emulsion is stable without agitation for at least three months.  
20       3. A process according to claim 1 or claim 2 in which the oil-in-water emulsion consists essentially of dialkyl thionocarbamate collector, emulsifier and water.  
4. A process according to any preceding claim in which the emulsion comprises dialkyl thionocarbamate collector in  
25       an amount of from 35 to 70% by weight of emulsion.  
5. A process according to any preceding claim in which the dialkyl thionocarbamate collector is isopropyl ethyl thionocarbamate.  
6. A collector composition which is an emulsion of  
30       dialkyl thionocarbamate collector in water and which comprises 5 to 95wt% dialkyl thionocarbamate collector, 1 to 30wt% emulsifier and 5 to 95wt% water, based on total emulsion.  
7. A collector composition according to claim 6 having  
35       any of the additional features recited in claims 2 to 5.



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB-97/00071

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 B03D1/012

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B03D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU 576 872 B (THIOTECH) 8 September 1988 cited in the application see page 3, line 5 - page 4, line 14 see page 6, line 11 - page 8, line 11 see example 3	1,5,6
A	US 4 211 644 A (A. WIECHERS) 8 July 1980 cited in the application see column 1, line 5 - line 42 see column 2, line 56 - line 59	1,6
A	US 4 526 696 A (R. DELOURME) 2 July 1985 cited in the application	
A	US 3 925 218 A (D. EDWIN) 9 December 1975 cited in the application	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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